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THE CATALYTIC PREPARATION OF HYDROXYLAMINE

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY Valentine Austin Jones
ENTITLED The Catalytic Preparation of Hydroxylamine

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF Master of Science

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In Charge of Thesis

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Committee

on

Final Examination*

*Required for doctor's degree but not for master's



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The Catalytic Preparation of Hydroxylamine.

I. Introduction.

The question of procuring a good yield of Hydroxylamine by a simple and inexpensive method has been the subject of considerable investigation by chemists for many years. A few methods have been suggested and used for its preparation, but in all the yields are not good, and the methods of separation from by-products are difficult and not conducive to complete separation. Reduction of nitrites, nitric acid and nitric oxide to Hydroxylamine by such reducing agents as sulphurous acid, chromous chloride, hydrogen sulphide, hydrogen, etc., have been attempted with but indifferent success, mainly, because of the fact that a good method of separation was lacking or that the reduction did not stop at Hydroxylamine, but continued further to give nitrous oxide, nitrogen or ammonia.

It was noticed by Victor Meyer and others that often some substance used as a catalyser or by-products of the reactions would cause the immediate decomposition of any Hydroxylamine which might be formed. The urgent need of a catalyser which could be used to facilitate the reduction of nitric oxide to Hydroxylamine alone and still not cause the decomposition of the Hydroxylamine formed, seems a paramount necessity if we expect to obtain Hydroxylamine in nearly theoretical amounts.

II. Historical.

In 1834 Faraday¹ published an article wherein he described some experiments on the use of platinum sponge as a catalyser. Among the reactions he experimented with was the reduction of nitric oxide by means of hydrogen using the platinum sponge as a catalyser. He passed a mixture of hydrogen and nitric oxide slowly over platinum sponge at room temperature. Reduction of the nitric oxide took place but his final product was not Hydroxylamine as he expected but ammonia and water. F.Kuhlmann² and Jouve³ also working on the reduction of nitric oxide by hydrogen with the use of platinum sponge as a catalyser obtained ammonia and water as the final product, altho Jouve working at temperatures not exceeding 115°C, claims to have obtained 1-2% of Hydroxylamine.

Cooke⁴ working with a mixture of nitric oxide and hydrogen and using platinum sponge as a catalyser, states that he obtained ammonia, Hydroxylamine and nitrous oxide, the amounts of which he does not mention in his paper. He states that if one uses nitric oxide and hydrogen in the volume ratio of 1:2, the following reaction will take place



and for 2 volumes of nitric oxide and 8 volumes of hydrogen the equation is



Sabatier and Senderens,⁵ Neoglie and Adhicary⁶ used nickel and copper as catalysers. They passed a mixture of nitric oxide and

hydrogen thru a glass tube which contained finely divided nickel or copper at temperatures ranging from 150-250°C. The resulting product was ammonia and nitrogen.

According to Divers and Haga,⁷ Dummreicher⁸ and Chesneau,⁹ Hydroxylamine and ammonia are produced when nitric oxide is passed thru a series of gas-washing bottles containing tin and conc. hydrochloric acid.. The yields, however, are small and the separation of the Hydroxylamine hydrochloride is not easily accomplished.

Chesneau⁹ experimenting with a solution of chromous chloride claims to have reduced nitric oxide to Hydroxylamine and ammonia. He points out that a rapid constant amount of nitric oxide must be passed into an acid solution to form Hydroxylamine, otherwise a slow stream will cause the formation of ammonia.

Ludwig and Hein,¹⁰ Divers and Haga¹¹ published papers in which they state that Hydroxylamine can be obtained in considerable amounts if nitric oxide is passed slowly into a heated mixture of tin and hydrochloric acid. They do not state the yields obtained by this method.

Chromous chloride solution according to Chesneau and Kohl-schutter¹² reduces nitric oxide to ammonia in neutral solutions while in acid solution it reduced to Hydroxylamine. The same authors also found that hydroiodic acid reduces nitric oxide to ammonia and nitrous oxide.

Dummreicher¹³ reports that stannous chloride in strongly acid solution will reduce nitric oxide to Hydroxylamine in small amounts and not readily.

Hans Ziehl¹⁴ attempted to prepare Hydroxylamine by the reduc-

tion of nitric oxide using a colloidal solution of platinum, which he prepared by reducing a slightly alkaline solution of chlor-platinic acid with hydrazine and adding a small amount of gum arabic. Equal volumes of hydrogen and nitric oxide were passed under pressure into a pressure bottle containing the colloidal platinum. The bottle is connected to a shaking devise and shaken vigorously. Ziehl found that no Hydroxylamine was formed by this method but that his final product consisted of ammonia and nitrogen. A mixture consisting of 2 volumes of nitric oxide and 3 volumes of hydrogen was tried but as before he obtained ammonia and nitrogen. They found that 82.64% of the nitric oxide was changed to nitrogen while 15.73% became ammonia.

Divers and Haga¹⁵ have succeeded in obtaining Hydroxylamine in the following manner. If sodium sulphide and sodium nitrite in solution are mixed, then acidified and boiled, Hydroxylamine is formed, and when the sulphide is in the proportion of 2 mols to 1 mol of the nitrite, and the hydrochloric acid added very slowly, almost all of the nitrogen is found on titration with iodine to have been converted into Hydroxylamine.



On evaporating the acid solution, separating the sodium salts by absolute alcohol and evaporating again, Hydroxylamine sulphate separates out. Further experiment proved that sodium meta-sulphide used with sodium nitrite gave the best yield of Hydroxylamine sulphate.

In 1887 Raschig reported that Hydroxylamine can be gotten from a nitrite by sulphonation followed by hydrolysis. Divers

and Haga²⁰ working on the suggestion given by Raschig's work used a concentrated solution of 2 mols of commercial sodium nitrite, 1 mol of sodium carbonate and then treated the solution with sulphur dioxide until just acid, while it was kept well agitated at 2-3°C below zero. It was claimed by them that at this temperature sulphur dioxide will not act on Hydroxylamine but will reduce the nitrite completely. At this temperature the conversion of the nitrite into oximido-sulphonate $\text{NaO-N} \begin{array}{c} \text{O} \\ \diagup \text{S} \diagdown \\ \text{O} \end{array} \text{O}_2\text{Na}$ appears to be complete. When gently warmed with a few drops of sulphuric acid, the oximido-sulphonate rapidly by hydrolysis, with marked rise in temperature into oxyamido-sulphonate and sodium acid sulphate. The solution of the salts is kept at 90-95°C for two days, by the end of which time all the oxyamido-sulphonate will have hydrolysed into Hydroxylamine sulphate.

B.B. Adhikary²⁰ in writing on the reduction of nitric oxide by contact action of metals and metallic oxides states that he passed a mixture of nitric oxide and hydrogen over gold, silver, magnesium, tin, antimony, bismuth and iron at various temperatures and in all cases ammonia and water were the final products.

E.P. Schoch and R.H. Pritchett²¹ after trying various other methods found that the preparation of Hydroxylamine by the electrolytic reduction of nitric acid according to the method of Julius Tafel²², to produce the largest yields. The apparatus used was identical with that of Tafel's except that the anode is a lead rod or pipe about one inch in diameter; this was used in place of the graphite anode employed by Tafel, because they found it necessary to use dilute sulphuric acid in the anode compartment. The Hydroxyla-

mine hydrochloride was freed from the accompanying ammonium chloride produced, by extraction with cold absolute alcohol. They claim to have obtained about 80% of the theoretical amount possible.

Other work too numerous to mention has been done upon the preparation of Hydroxylamine, but the methods are only of theoretical importance and therefore will not be mentioned here.

III. Purpose of Work.

As it will be seen from the preceding pages, very few experiments have been performed using a catalyst for promoting the reduction of the nitric oxide to Hydroxylamine. In view of the difficult methods used for recovering Hydroxylamine from the by-products by the reaction it was deemed that, if possible, some method might be devised for preparing Hydroxylamine by the use of two gases, one of them to be nitric oxide and the other some reducing gas as sulphur dioxide, hydrogen, hydrogen sulphide, etc., in the presence of a catalyst. In this manner interfering by-products would be eliminated and the Hydroxylamine easily and quickly separated. It will be noticed from Ziehls and Sabatier and Senderens (loc. cit.) work using colloidal platinum and nickel respectively, that the reduction does not stop at Hydroxylamine but continues to ammonia. To secure a catalyst which would promote the reduction of nitric oxide to Hydroxylamine and stop there, seemed to be the key to the solution of this problem, so it was thus made the object of this paper. It was

thot advisable to undertake various methods of reduction and determine the effect different catalyist had on the reaction. Once the reduction of nitric oxide to Hydroxylamine was accomplished, a method of separation and purification would be a comparatively simple task because of the absence of interfering substances.

Altho Schoch and Pritchett (loc.cit.) have obtained Hydroxylamine by the electrolytic reduction of nitric acid and claim to have obtained as much as 80% of the theoretical yield, we did not attempt to obtain Hydroxylamine by an electrical method but have confined ourselves to its production by strictly chemical means.

The method to be used for the detection Hydroxylamine was the reduction of Fehling's solution. Very minute amounts of Hydroxylamine or its salts are sufficient to cause the formation of the brown copper oxide.

IV. Experimental.

According to Sabatier and Senderens (loc.cit.) the activity of nickel as a catalyist is nil at low temperatures, but at 250-300° C nickel is quite active. It was decided to see if nickel at a temperature of 100-115°C would catalyse the reduction of nitric oxide to Hydroxylamine, and not to ammonia. The apparatus used is shown on Figure 1.

Preparation of Catalyser.—The catalyser was made by melting nickel nitrate in its own water of crystalization in a nickel cruci-

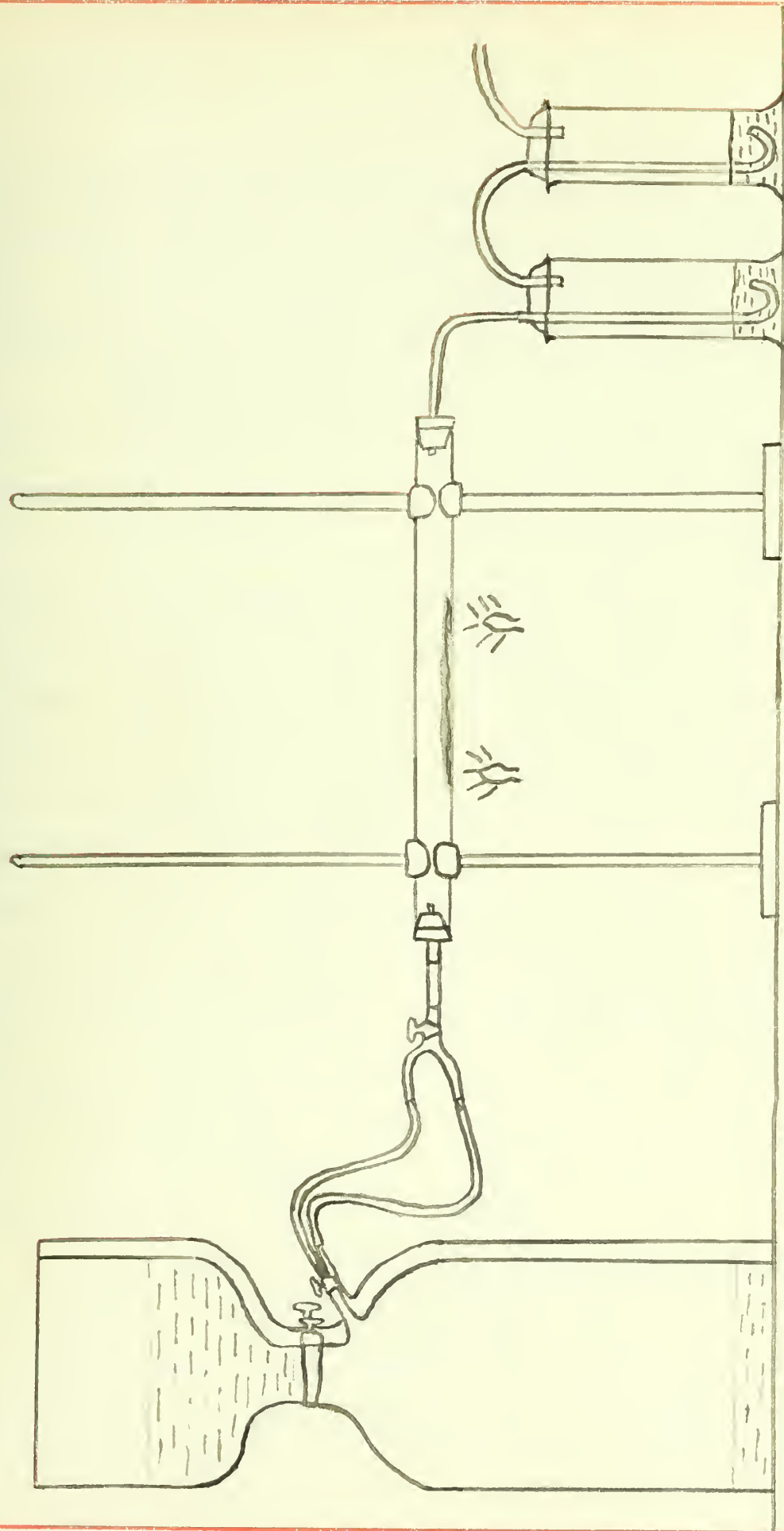


Figure #1

ole and then impregnating animal charcoal with the solution. The impregnated charcoal was then heated in the crucible to form the nickel oxide. It was placed in a glass combustion tube heated to $250-300^{\circ}\text{C}$, and reduced with a stream of hydrogen for three hours.

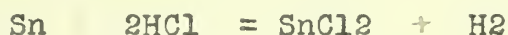
Procedure -- The tube, after the reduction of the nickel oxide had taken place, was allowed to cool slowly to 105°C with hydrogen still passing thru. A mixture of 2 volumes of hydrogen and one volume of nitric oxide was slowly passed thru the tube, the temperature being maintained about 110°C , the alkaline gases produced were absorbed in dilute hydrochloric acid. When the run was completed this acid solution was examined for Hydroxylamine by adding a little of the solution to Fehling's solutions. No reduction of the Fehling's solution occurred which proved the absence of Hydroxylamine. On opening the tube it was found to smell very strongly of ammonia. The hydrochloric acid solution was evaporated to dryness on a water bath, the residue broken up and again tested for Hydroxylamine and ammonia. No Hydroxylamine hydrochloride was found to be present but on heating a little of the residue with sodium hydroxide, the odor of ammonia was easily detected. Another run was made using equal volumes of nitric oxide and hydrogen but as before ammonia was the final product.

A statement is found in many text books that Hydroxylamine can be prepared by passing nitric oxide thru a solution of tin dissolving in hydrochloric acid. No mention, however, is made in regards to the amounts obtained and so in order to get some idea

of the yield of Hydroxylamine produced, by this method, it was decided to repeat the procedure using metallic mercury as a catalyser.

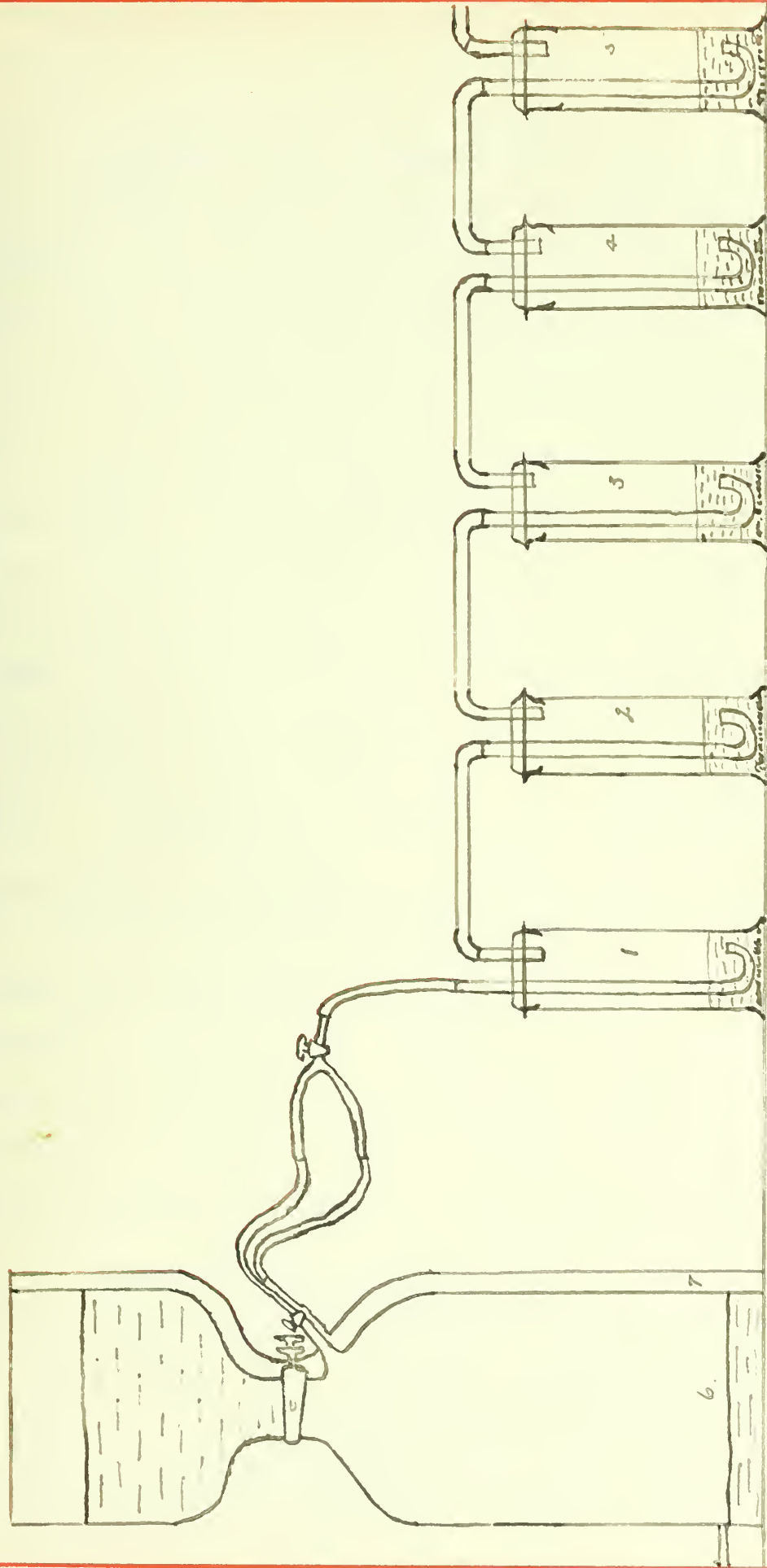
Procedure--The apparatus is shown in Figure 2. In each of the gas washing bottles was placed tinfoil cut into very small squares, and covered with a dilute solution of hydrochloric acid.

The two gases nitric oxide and hydrogen in equal volumes were bubbled thru the bottles at a uniform rate of approximately 30 bubbles per minute. The tin in dissolving gives up nascent hydrogen according to the equation



which was expected to reduce the nitric oxide while stannous chloride and mercury might catalyse the reduction. After fourteen liters of each gas had been passed thru the bottles, the solutions from each of the bottles were combined in a large Erlenmeyer flask, water added and the tin precipitated out with hydrogen sulphide. Two precipitations were necessary to separate all of the tin. The solution was then filtered, washed and the filtrate evaporated to dryness on a water bath. The residue was examined for Hydroxylamine but no reduction of Fehling's solution occurred. It was then tested for ammonia which was found to be present. Mercury being omitted another run similar to the first gave ammonia as the only product.

It was apparent from the preceding experiments that if satisfactory yields are to be obtained a more intimate and longer contact should be made between the gases and the catalyser. With this idea in mind an apparatus as shown in Figure 3, was constructed.



1, 2, 3, 4, 5 are gas-washing bottles.

6, 7 are gasometers containing NO.

Figure # 2

Apparatus--This consisted of an tight cast iron cylinder about 3 feet tall and 8" in diameter. The valve at the top was used to regulate the flow of the gases while the one at the bottom was connected with the water main by means of which, water could be forced in compressing the gases to any required pressure up to 40#. By means of a hollow copper tube bent in spiral shape the gases could be connected to a pressure bottle which was mounted on a shaking devise. Nitric oxide was prepared by mixing in a flask, 200 grams of ferrous sulphate with 40 grams of potassium nitrate and dropping hot dilute sulphuric acid on the mixture, the gas evolved being collected in gasometers. The gas cylinder was filled with water, the hollow copper tube connected with the gasometer and the gas forced in under a water head contained in a connecting gasometer. The valve at the bottom of the cylinder being opened simultaneously with the valve at the top. After twelve liters of nitric oxide had been forced in both valves were closed and connection made with a hydrogen tank. The upper valve was then opened and hydrogen forced in until the gauge on the cylinder showed 25# pressure, after which the valve was closed. In the pressure bottle was placed a colloidal solution of platinum prepared according to directions given by H.L. Lockte of the University of Illinois.

Preparation of Catalyst--About .3 gram of platinum was dissolved in aqua regia and evaporated to dryness twice, then taken up with hydrochloric acid. The chlor-platinic acid thus formed was poured into a beaker containing 250 c.c. of water made slightly alkaline with sodium hydroxide.

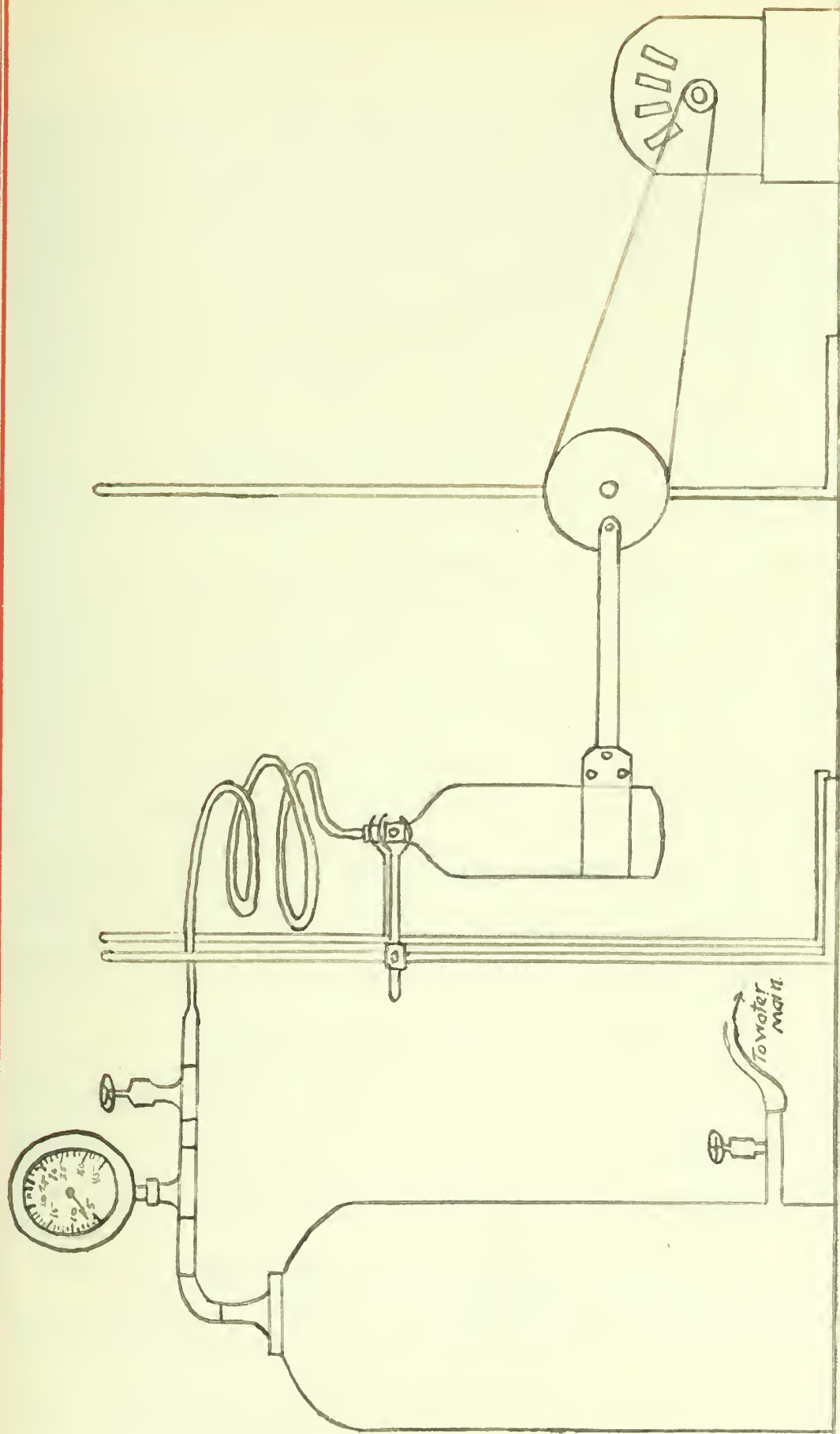


Figure #2

Approximately .3 gram of gum arabic in water solution was added, and a few crystals of hydrazine hydrochloride were dropped into the solution. Reduction took place almost immediately after which the solution was made acidic with hydrochloric acid. The solution was poured into the pressure bottle, the bottle evacuated and connection made to the gas cylinder.

Procedure--The motor was started and the solution shaken for six hours during which time the reading on the gauge was carefully noted. No decrease on the gauge reading was observed during the run. The bottle was then disconnected and the solution poured into a flask containing a volume of acetone equal to that of the solution. This acetone solution was allowed to stand overnight and then filtered to remove the precipitated platinum. The filtrate was then tested for Hydroxylamine with Fehling's solution, but no reduction was observed. On evaporating the solution to dryness no residue was left proving that nitric oxide and hydrogen in the presence of colloidal platinum would not react.

Platinum as the Catalyst--A active form of platinum has been developed in the organic division of the University of Illinois, which has been very successful in reducing many organic compounds. It was thought that it might also promote the reduction of nitric oxide.

Preparation of the Catalyst--About .4-.5 gram of platonic chloride was dissolved in a mixture of 5 grams of sodium nitrate

and 4 grams of potassium nitrate and the mixture evaporated to dryness on a water bath. It was then fused to a quiet liquid and allowed to cool, after which it was dissolved in water and filtered. The platinum precipitate on the filter paper was washed with water until free from salts. It was then washed into the pressure bottle and the filter paper saved to be used again to filter off the platinum after the run was completed.

Procedure--The solution in the pressure bottle was made acid with hydrochloric acid, the bottle evacuated and connections made. The bottle was shaken for six hours, the solution removed, filtered and evaporated to dryness. No residue was left showing that the platinum used as a catalyser did not have any effect in aiding hydrogen reduce nitric oxide.

Mercury as the Catalyst--Using the same pressure apparatus as previously described, 15 grams of mercurous chloride and 20 grams of stannous chloride were placed in the pressure bottle and 200 c.c. of water containing 15 c.c. of dilute hydrochloric acid were added. The bottle was evacuated and connections made with the gas cylinder. The bottle was shaken for six hours and the gauge reading carefully observed. The mercurous chloride was reduced to black metallic mercury by the stannous chloride. It was thought that the stannous chloride in conjunction with the hydrogen formed by the reaction would act as a reducing agent in the presence of metallic mercury as the catalyst. The gauge reading showed no decrease after the six hours. The solution was removed from the flask, almost neutralized by sodium hydroxide and the tin

precipitated out by hydrogen sulphide. A small amount of the mercury was also precipitated by the hydrogen sulphide but the major amount was removed when the solution was filtered. The solution was then evaporated to dryness on a water bath and the residue tested for Hydroxylamine. The residue was composed completely of sodium chloride, no Hydroxylamine or ammonia being formed.

Reduction by Chromous Chloride--Chesneau and Kohlschutter (loc.cit.) in their paper on the reduction of nitric oxide by means of chromous chloride found that when nitric oxide was passed into a neutral solution of chromous chloride that ammonia would be the final product while in an acid solution Hydroxylamine would be formed. They state, however, that nitric oxide must be passed into the acid solution of chromous chloride in order to secure Hydroxylamine, otherwise ammonia would be formed. A run was therefore made using chromous chloride in an acid solution as a reducing agent.

Preparation of the Chromous Chloride--Metallic chromium was ground up to a fine powder and 100 c.c. of water and 50 c.c. of hydrochloric acid added. The mixture was then poured quickly into the pressure bottle which was then evacuated and connections made with the gas tank.

Procedure--The bottle was shaken for ten hours after which time the solution was removed, filtered and made alkaline with sodium hydroxide which precipitated all of the chromium. This was filtered off and the solution tested for Hydroxylamine. No reduction of the Fehling's solution took place. The solution was evaporated slightly,

then made acidic, evaporated to dryness, and again tested for Hydroxylamine. After a negative result had been obtained it was tested for ammonia which was found to be present in considerable amounts. It is evident that the chromous chloride caused the reduction to proceed to ammonia and not to Hydroxylamine. It was that, however, in view of Chesneau and Kohlschutter's work that some Hydroxylamine should have been formed. In order to ascertain if the above authors really secured Hydroxylamine as they claim, their work was repeated. The apparatus used is shown in Figure 4. Nitric oxide from a gasometer was passed rapidly into an acid solution of chromous chloride protected from air by a layer of petroleum ether. The residual gas was collected in another gasometer and again passed thru the chromous chloride solution. This procedure was repeated several times, until a marked decrease in the volume of nitric oxide was observed. The solution was poured into a separatory funnel and the chromous chloride solution drawn off. It was then made alkaline with sodium hydroxide and the precipitated chromium filtered off. The filtrate was evaporated to dryness and the residue tested for Hydroxylamine. No reduction of the Fehling's solution took place. It was then examined for ammonia which was again found to be present in considerable amounts.

The experiment was again repeated, all possible care in following directions was taken, samples of the chromous chloride solution being tested every few minutes, but at no time could any positive test for Hydroxylamine be obtained. Altho Chesneau and Kohlschutter claim to have obtained Hydroxylamine in this manner,

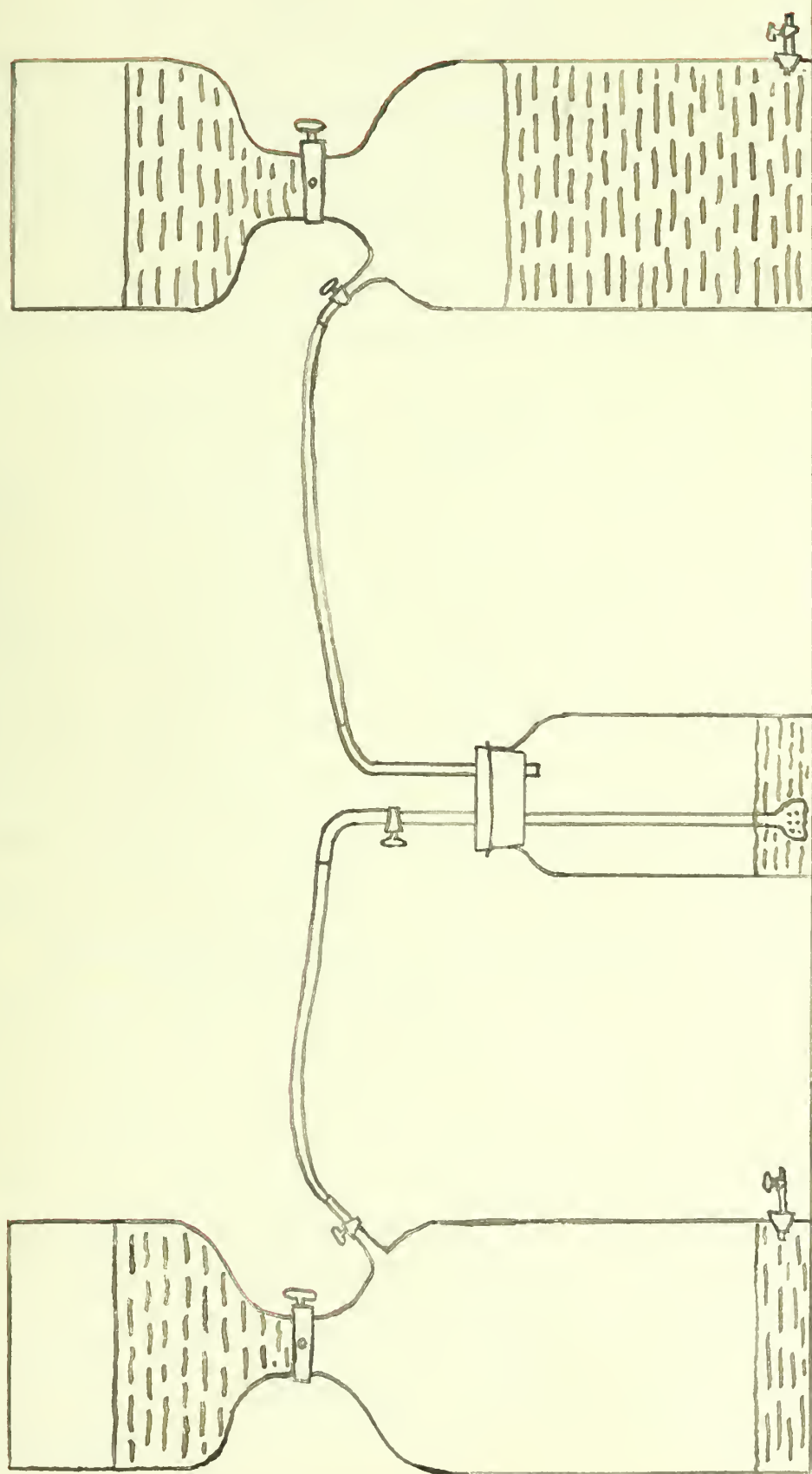


Figure #4

we do not believe it possible that Hydroxylamine could be formed and stay in the solution as Hydroxylamine in the presence of such a powerful reducing agent as chromous chloride. It may be possible that Hydroxylamine is formed as an intermediate product, but our belief is that it is immediately reduced to ammonia.

Nickel as the Catalyser--In view of previous research and our own results, it was decided that the platinum group could not be used as catalysers due to the fact that Hydroxylamine will decompose in the presence of colloidal platinum and platinum black. In a paper published by A. Findlay and W. Thomas the products of the decomposition are said to be ammonia nitrogen and nitrous oxide. B. Adhikary (loc. cit.) did all his work at temperatures over 100 C. A search of the literature failed to reveal any statements regarding the use of lower temperatures. If at over 100°C nickel changes nitric oxide to ammonia, would it not be possible at temperatures up to 90 C that the reducing action would not be so strong and instead of reducing the nitric oxide to ammonia it might stop at Hydroxylamine?

Preparation and Use of the Catalyst--A nickel catalyst which had been prepared by reducing nickel nitrate, was put into the pressure bottle, water added, the bottle evacuated and connected to the gas cylinder. After opening up the cylinder valve, the bottle was shaken for three hours at ordinary temperature. No decrease could be observed in the gauge reading. The temperature of the solution was raised gradually by placing a small flame under the bottle and surrounding the shaking bottle by an asbestos box to keep the heat in. A temperature of about 80-90 C could be obtained in this manner.

The bottle was shaken for three more hours, the flame removed and the bottle with solution allowed to cool while shaking. The solution was filtered to remove the nickel, and a small amount of hydrochloric acid added to the filtrate. The latter was evaporated to dryness but no residue was left showing that at temperatures below 100 C nickel did not catalyse the reduction of nitric oxide in a water solution.

Reduction by Means of Red Phosphorus--Among the chemical properties of red phosphorus is listed the fact that concentrated nitric acid is reduced with almost explosive violence while dilute nitric acid evolves nitrous fumes in the presence of red phosphorus. Because of the reducing action it appeared possible that the red phosphorus might also reduce nitric oxide. A mixture of the red phosphorus and water was put into the reaction bottle and nitric acid bubbled thru the solution. In conjunction with this method, red phosphorus and water were also put in the pressure bottle, connection made with the gas cylinder and the bottle shaken for three hours. The nitric oxide in the gasometer was passed back and forth several times thru the reaction bottle. The solutions were taken from the reaction and pressure bottles, filtered and evaporated to dryness after 10 c.c. of hydrochloric acid had been added. No residue is left proving red phosphorus would not cause the reduction of nitric oxide. In another run potassium iodide was added as a catalyser, but the result was similar to the first as no Hydroxylamine was obtained.

The Use of Sodium Amalgam as the Reducing Agent--The reduction of many organic compounds by sodium amalgam led to the belief that it might aid in the reduction of nitric oxide. An amalgam containing .214% sodium was put into the pressure bottle, connections made and the bottle shaken for eight hours. It was removed from the bottle, filtered to remove the amalgam, a small amount of hydrochloric acid added and the solution evaporated to dryness. No residue was obtained.

Catalytic Reduction by Means of Palladium Asbestos-----

Sabatier and Senderens have shown that in the presence of palladium sponge previously saturated with hydrogen, nitric oxide is completely converted into water and ammonia. Their work was repeated by us with the exception that instead of palladium sponge being used we worked with palladium asbestos. The two gases, nitric oxide and hydrogen were preheated before passing over the catalyst. A diagram of the apparatus is shown in Figure 5. Nitric oxide and hydrogen were passed thru gas-washing bottles containing sulphuric acid and then thru a short piece of heavy glass tubing about three-fourths of an inch in diameter, where they were heated slightly. The preheated gases were then passed thru the catalyser tube containing the palladium into a dilute solution of hydrochloric acid. On examination of the hydrochloric acid solution it was found to contain ammonium chloride only, no Hydroxylamine being formed.

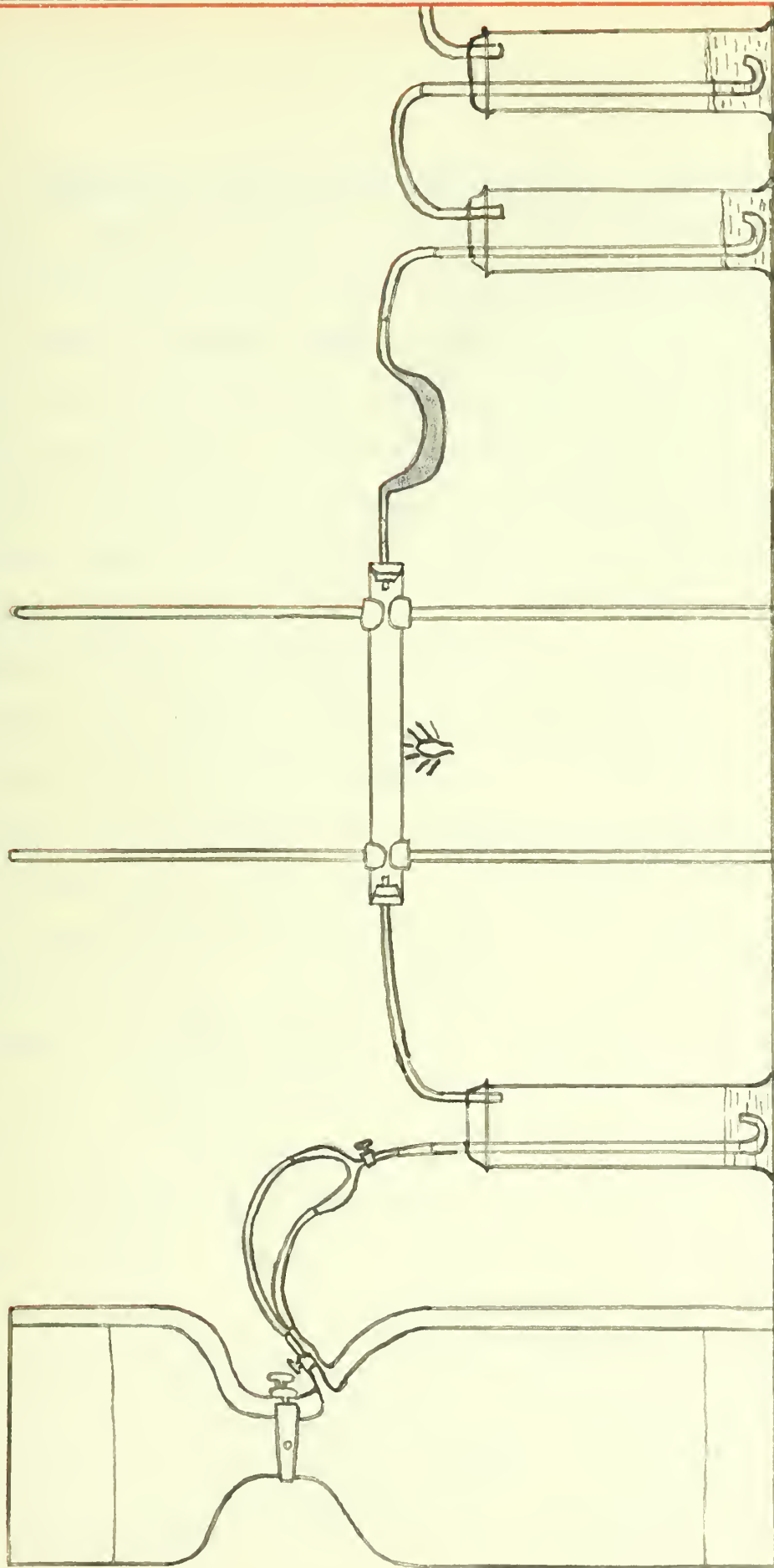
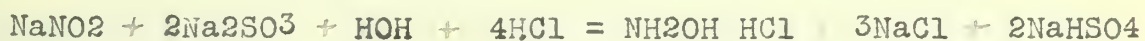


Figure #5

Reduction by Use of Sulphur Dioxide--In Divers and Haga

(loc.cit.) publication, state that they have obtained Hydroxylamine using sodium nitrite and sodium sulphite according to the equation.



It would seem from the above equation that sulphur dioxide is the active reducing agent. Tanatar²⁵, however, claims that sulphur dioxide will attack Hydroxylamine reducing it to ammonium sulphate. Divers and Haga's method was repeated by us, all directions being carefully followed. Sodium nitrite and sodium sulphite were mixed in the proportions as given by the equation, water added and the hydrochloric acid added very slowly. The solution was evaporated to dryness, an absolute alcohol extraction made but no Hydroxylamine was found to be present. The method was again repeated but as before no test for Hydroxylamine could be obtained. It was noticed that on each addition of the hydrochloric acid a sharp rise in temperature followed. To determine if this rise in temperature was the cause of the non-formation of Hydroxylamine, the flask was placed in an ice-salt bath about -10°C . The hydrochloric acid was added very slowly to the solutions of the salts and at no time was the temperature above -5°C .

The solution was then placed in evaporating dishes and evaporated to dryness. Before evaporation the solution was boiled for an hour to expell as much as possible of the sulphur dioxide. On testing the residue, Hydroxylamine was found to be present, It was extracted with absolute alcohol and the alcohol distilled off, leaving a small amount of Hydroxylamine sulphate as a residue. The separation of Hydroxylamine sulphate from the by-products, sodium chloride

and sodium acid sulphate is not complete because of the tendency of these salts to occlude small amounts of Hydroxylamine sulphate. Several extractions are necessary to completely remove all the Hydroxylamine sulphate. It is important to note that unless the reaction is carried out at low temperatures and the hydrochloric acid added very slowly, no Hydroxylamine sulphate will be formed. A possible explanation for this fact is that at room temperatures, sulphur dioxide will attack the Hydroxylamine formed and convert it into ammonium sulphate, while at temperatures below 0°C , sulphur dioxide will complete the reduction but will not act on the Hydroxylamine formed.

Since Hydroxylamine can be formed by the reduction of a nitrite, would it not be possible that nitric oxide could be reduced in a similar manner? On account of the very slight solubility of nitric oxide in water, advantage was taken of the fact that nitric oxide will form an addition compound with ferrous sulphate in water solution. An apparatus such as shown in Figure 6, served the purpose very well. About 8-10 grams of ferrous sulphate was dissolved in 600 c.c. of water and the solution poured into a large wide-mouthed bottle. Nitric oxide made from ferrous sulphate, potassium nitrate and dilute sulphuric acid was passed into the water solution until it became a dark brown color. Sulphur dioxide made by dropping sulphuric acid on sodium bisulphate was also passed into the water solution. The bottle was then immersed in an ice-salt bath and the solution stirred vigorously with a glass stirrer.

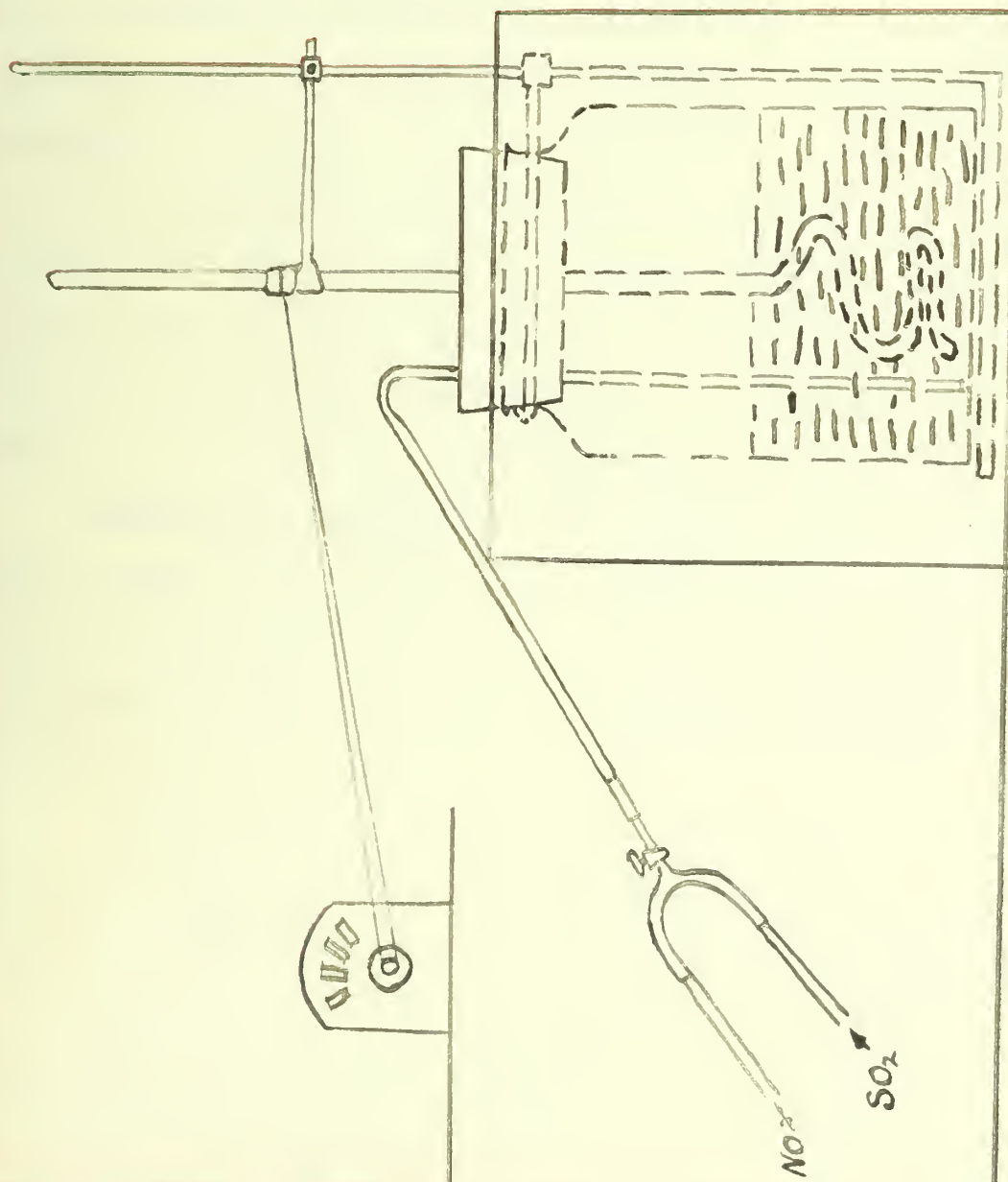


Figure #6

Approximately 10 liters of nitric oxide and 15 liters of sulphur dioxide were passed into the solution. After shaking for an hour the solution turned to a white color. It was then removed, allowed to come to room temperature. A small amount of the solution was tested with barium chloride, which gave a white precipitate showing that the sulphur dioxide had been oxidized to sulphuric acid. Sodium hydroxide was added to precipitate all the iron and the solution filtered. The filtrate was made acidic with sulphuric acid and evaporated to dryness. No test for Hydroxylamine was obtained.

In all probability Hydroxylamine was immediately reduced by the ferrous sulphate or by the sulphur dioxide. According to Tanar (loc.cit.) when a solution of Hydroxylamine sulphate is saturated with sulphur dioxide, kept over night and evaporated to dryness on a water bath, ammonium sulphate is formed.

Reaction with Hydrazine--To ascertain whether hydrazine would reduce nitric oxide, about 10 grams of it in water solution was put into a bottle and nitric bubbled thru. Examination of the solution proved that no reduction had taken place.

V. Discussion.

It will be seen from our results that the preparation of Hydroxylamine by a strictly chemical method is difficult and, in many cases, without success, the direct cause of the failure to produce Hydroxylamine by some of the methods tried was due mainly to the great susceptibility of Hydroxylamine to the action of many substances which either decompose it as quickly as it is formed or reduces it at once to ammonia.

It should be noted that low temperatures are conducive to the production of Hydroxylamine, higher temperatures causing the formation of ammonia, nitrogen and nitrous oxide. This fact prohibits the use of such catalyists as nickel, copper, iron, etc., which require temperatures over 100° C before they become active and thus our work was confined to the use of the platinum group. It was shown that nickel in a water solution at 80-90 C does not cause the reduction of nitric oxide. The action of the catalyst used in this research either caused the decomposition or reduction of the Hydroxylamine formed or else had no effect on the reaction. No catalyser has been found which would promote the reduction to Hydroxylamine and not to ammonia.

Hydroxylamine sulphate was obtained us using Diver's and Haga's (loc.cit.) method, but the amount obtained was small and a complete extraction difficult. The attempt to reduce nitric oxide by sulphur dioxide in the presence of ferrous sulphate as might have been expected because of the action of both ferrous sulphate and sulphur dioxide in decomposing any Hydroxylamine formed.

If it were possible to procure some substance, the addition of which, would cause the Hydroxylamine to be precipitated as soon as it were formed, the solution of this problem might be solved.

VI. Summary.

I. Nitric oxide will not be reduced in the presence of colloidal or finely divided platinum used as a catalyst.

II. At temperatures below 100°C nickel is not active while at higher temperatures it will promote the reduction of nitric oxide to ammonia.

III. Strong reducing agents such as chromous chloride reduce nitric oxide to ammonia, no Hydroxylamine being formed.

IV. Salts of Hydroxylamine in a saturated solution of sulphur dioxide and in the presence of ferrous sulphate are reduced to ammonia, if allowed to stand at room temperature for several hours.

V. Substances such as metallic mercury, red phosphorus, sodium amalgam, stannous chloride, and hydrazine do not cause the reduction of nitric oxide to proceed to the formation of Hydroxylamine.

VII. Bibliography.

1. Faraday: Pogg. Ann. 33-149 (1834).
2. F.Kuhlmann: A. 29,286, (1839).
3. Jouve: Comp.rend. 128,435, (1899).
4. Cooke: C.1327, (1888).
5. Sabatier and Senderens: Comp.rend. 135,278, (1902).
6. Neogle and Adhicary: C. 463, (1911).
7. Divers and Haga: J.Chem.Soc. 47,623, (1899).
8. Dummreicher: W.Ak.B. 82,560, (1880).
9. Chesneau: C.R. 129,100, (1899).
10. Ludwig and Hein: B.2,671, (1869).
11. Divers and Haga: J.Chem.Soc. 47,623. (1885).
12. Chesneau and Kohlschutter: B. 37,3093,(1904).
13. Dummreicher: Abstract J.Chem.Soc. 361, (1882).
14. H.Ziehl: Doctor's Thesis "Katalytische Hydrierung von Stickstoffverbindungen. Gottingen. (1914).
15. Divers and Haga: J.CHEM,SOC. vol.LI. 660,(1887). Trans.
16. Divers and Haga: J.CHEM.SOC. vol.69,1665, (1896) Trans .II.
17. Raschig: Chem.Zeit. 12,219, (1887).
18. Divers and Haga: J.CHEM.SOC. Trans. 1665, (1896).
20. B.B.Adhikary: Chem.News, 112, 163-4 (1915).
21. Schoch and Pritchett:J.Am.Chem.Soc. 2042-4, (1916).
22. J.Tafel: Z.Anorg.Chem. 31, (1902). 289, (1902).
23. Tanatar: B. 32,241-4 (1899).

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